



Application of Activated Carbon and Natural Zeolite for Phosphate Removal from Laundry Wastewater

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ABSTRACT

The number of laundry industry has been increasing rapidly which influences the amount of detergent usage in the washing process. Generally the laundry industries dump their wastewater directly to environment without any treatment. Phosphate contained in detergent shall accumulate in the environment then finally would cause eutrophication where the water body becomes rich of dissolved nutrient which effects the dissolved oxygen contained in water body. One of wastewater treatment methods is adsorption. Two different kinds of adsorbents were applied in this investigation namely activated carbon and natural zeolite. Synthetic laundry wastewater was used in order to control the phosphate concentration. The objective of this experiment was to study the removal of phosphate concentration of each adsorbent filled in adsorption column by using circulation method. The column has 1 inch of diameter, 50 cm of height, and 50 ml/minute of flowrate. The concentration of phosphate was varied between 2-8 mg/l whereas the adsorbent height in the column was varied between the ranges of 10-40 cm. The size of both adsorbents was 10 mesh. It was found that the natural zeolite was superior to remove the phosphate compared to activated carbon. The highest phosphate removal of 90% was obtained by using 40 cm of natural zeolite height in the adsorption column when make use the phosphate concentration of 2 mg/l.

Keywords: phosphate, laundry wastewater, activated carbon, natural zeolite

1. INTRODUCTION

Laundry industries use detergent in the washing process, because detergent works better than soap in hard water. Increasing the number of laundry industries make the use of detergent increase as well. The primary substance in the detergent is *natrium tripoly-phosphat* that acts as builder and surfactant, so the wastewater from the washing process contain phosphate compound. However, at the mean time, almost all industries dump effluent from the process directly to the river or water body without any treatment. According to Palembang City Regulation No. 2 of 2003 on River Water Quality Standards and Wastewater Quality Standard, the maximum levels allowable phosphorus content is 2 mg/l and according to PP 82 of 2001 on water quality management and pollution control, the content of total phosphate as P allowed for class II of water is 0.2 mg/l.

Eutrophication is water pollution caused by the emergence of excess nutrients into the

aquatic ecosystem. Eutrophication occurs because of the chemical content of the phosphate (PO_4^{3-}). A water body is called eutrophication if the total concentration of phosphate into the water in the range of 35 – 100 $\mu\text{g/L}$. Actually the process of eutrophication requires a very long time (thousands of years), but due to the development of science and technology that underpin modernization is not accompanied by the wisdom of the environment, so in a matter of decades or years alone eutrophication can occur.

Some detergents contain relatively quite lot phosphates; therefore the detergent is also a source of eutrophication which needs special attention. Although many laws and regulations that restrict or prohibit the use of detergents containing phosphates, but until now there has not been an impact on the elimination of eutrophication problem.

Effect of moderate eutrophication in nutrient poor water is not negative, but if eutrophication continues resulting plankton growth to be very dense, so it will cover the water. This process



will lead to dark under the water surface, and the condition is harmful to benthic vegetation. Serious problems due to eutrophication caused by single-cell algae growth is great, the decomposition process of dead cells will reduce dissolved oxygen. Aquatic plants (including algae) will affect the O₂ concentration and pH of the surrounding waters. The rapid growth of algae will cause greater fluctuations in pH and dissolved oxygen. This will lead to disruption of metabolic processes in the organism, which can ultimately lead to death.

Eutrophication is a natural process and can occur in a variety of water body, but if there is contamination of phosphate materials due to human activities and takes place continuously, the eutrophication process will increase. Various methods have been investigated in order to remove the nutrients such as phosphate and ammonium. On the other hand, natural zeolite is potentially a cheap and abundant adsorbent suited for water and wastewater treatment. Compared with other adsorbent materials such as organic resins [1], zeolite offers a number of advantages including low-cost, excellent selectivity at low temperatures, the release of non-toxic exchangeable cations (K⁺, Na⁺, Ca²⁺ and Mg²⁺) to the environment [2], simple operation and easy maintenance [3]. Results showed that zeolite can be used to remove both ammonium and phosphate from aqueous solutions [4].

There are many natural zeolites identified in the world. Among the zeolites clinoptilolite is the most abundant natural zeolite and is widely used in the world. In zeolite structure, three relatively independent components are found: the aluminosilicate framework, exchangeable cations, and zeolitic water. The general chemical formula of zeolites is $M_x/n[Al_xSi_yO_2(x+y)] \cdot pH_2O$ where M is (Na, K, Li) and/or (Ca, Mg, Ba, Sr), n is cation charge; $y/x = 1-6$, $p/x = 1-4$ [5].

However, existing problem in detergent wastewater treatment particularly comes from laundry process is the absence of effective and efficient treatment systems by technically and economically. Treatment methods that have so far is coagulation and flocculation which require a lot of chemicals and biological methods that produce sludge that becomes another problem for the environment. The purpose of the research is to study phosphate removal of laundry industrial wastewater by using two different

types of adsorbents, namely activated carbon and natural zeolite.

In preliminary research, wastewater sampling was conducted at three different places of laundry industry. Samples were taken from the first wastewater washing process which contains a lot of clothes detergent, so the phosphate contained in the wastewater is the highest during the process of washing clothes. Results from the preliminary research indicate that all the three samples still meet the quality standard of wastewater except for test results of phosphate, TSS and pH, which for BOD, COD and fat & oil is still below the quality standards set by the government, but here we will only focus on the decrease of phosphate.

Based on preliminary research results, it were known the magnitude of phosphate concentration in each of the laundry wastewater are 4.2 mg/l, 4.0 mg/l and 2.3 mg/l which all exceed allowed thresholds and should be got prior treatment before being discharged into drainage. In this study the synthetic laundry wastewater was used, it is intended that researchers can adjust the concentration of phosphate to be applied.

2. METHODS

The synthetic laundry wastewater was made by dissolving detergent to obtain desired phosphate concentration. The wastewater is contacted with an adsorbent in circulation mode to decrease the amount of phosphate contained. Preparation of artificial wastewater was preceded by weighing the amount of detergent phosphate adjusted to the desired concentration, and then dissolved in a volume of distilled water. This was done after knowing the phosphates content in the detergent. The phosphate contained in the detergent is 0.037 % of detergent mass

2.1 Chemicals and Materials

Activated carbon and natural zeolite of 10 mesh were used as adsorbent. The carbon was activated by means of soaked in 15% HCl solution (1:1) for 24 hours. Activated carbon was filtered and washed with distilled water until the water pH close to 7 (neutral). Once neutral, activated carbon was dried in an oven at 110°C for 15 minutes. Natural zeolite was activated by heating in a muffle furnace at a temperature of 300°C for 3 hours. The synthetic laundry wastewater was made by dissolve a certain weight of commercial detergent.



2.2 Characterization and Analysis

Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX) of JEOL JSM-6360/EDX type of 6510 LA was used to determine the topography (surface texture of the sample), morphology (shape and size), and composition (constituent elements) of the adsorbent. Surface Area Analyzer (SAA) was used to determine the surface area of the adsorbent by nitrogen gas adsorption method. Phosphate concentration was measured by using a HACH spectrophotometer.

2.3 Procedure

Experiment carried out by means of flow 250 ml of synthetic wastewater stream with phosphate concentration of 2 mg/l, 4 mg/l, 6 mg/l, and 8 mg/l at a flowrate of 50 ml/min in an adsorption column filled with activated carbon or natural zeolite. Then the wastewater circulates from the bottom to the top of the adsorption column up to 1 hour by using a pump. The column filled with the adsorbent of 10 cm, 20 cm, 30 cm and 40 cm height. Samples were taken after 1 hour and the phosphate concentration of the sample solution was measured by using a spectrophotometer.

3. RESULTS

3.1 Characterization

Table 1. EDX Carbon Analysis Results

No.	Elements	Percentage (%)	
		Before Activation	After Activation
1.	C	46.93	77.37
2.	Na	1.35	1.32
3.	Mg	0.70	0.22
4.	Al	9.12	2.95
5.	Si	10.39	5.39
6.	O	19.56	0.30
7.	Ca	1.68	1.68
8.	Ti	0.15	0.15
9.	Fe	2.49	2.81
10.	Cu	5.48	5.23
11.	K	1.83	1.10

Table 1 shows an increased on the Carbon elements (C) from 46.93% to 77.37%. While

other elements decreased, the Titanium (Ti) and calcium (Ca) elements did not change. The increase of the carbon percentage caused by the reduction in the percentage of other elements as impurities on the activated carbon, in which the impurities soluble in activator solution.

Table 2. EDX Natural Zeolite Analysis Results

No	Elements	Percentage (%)	
		Before Activation	After Activation
1.	Si	56	73
2.	Al	10.33	14.21
3.	Ca	3.0	3.0
4.	K	2.2	2.2
5.	Fe	2.0	2.0
6.	Mg	1.2	0.18
7.	Ti	0.5	0.27
8.	O	16.69	5.02

According to natural zeolite EDX analysis results, there is an increase in the percentage of Si and Al, this is caused by the reduction in the percentage of other elements as impurities such as Mg, Ti and O in the activated natural zeolite, in which the impurity elements in the natural zeolite may evaporate due to the physical activation of heating process, but other elements such as Ca, K and Fe was not changed suggesting the activation process has not occurred to the fullest. A little decrease in Si/Al ratio makes the natural zeolite more hydrophilic that will increase absorptive capacity of natural zeolite. From the Si/Al ratio, the natural zeolites include in moderat content of Si [6].

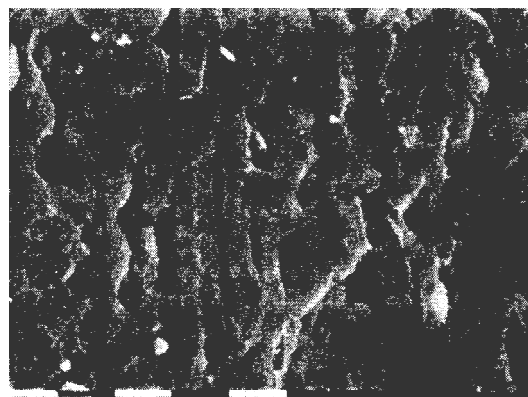


Fig. 1. SEM image of carbon before activated (1000x of magnitude)

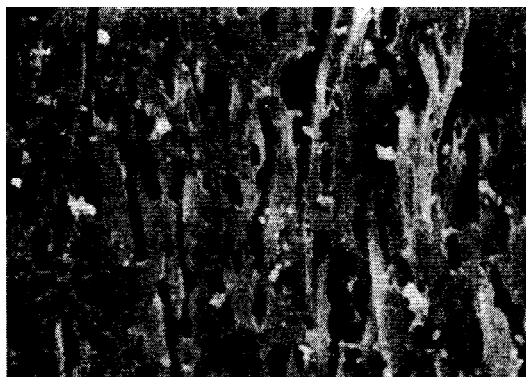


Fig. 2. SEM image of carbon after activated (1000x of magnitude)

As demonstrated in Figure 1 and Figure 2 there is a change in the carbon pores before and after activation, the open pores of carbon in Figure 2 is more than in Figure 1. This is because the soaking process of the activator solution (HCl 15%) resulted in impurities that were previously covered the pores of the carbon dissolved in the activator solution and leave the pores of carbon; this is resulting in no impurities that clog the pores of the carbon. With the opening of the carbon pore, adsorption ability of carbon will increase.

From the comparison between Figure 3 and Figure 4, it can see that there is a change in the zeolite pores before and after activated. After activated the surface of zeolite appear less sharp than before. Probably this is due to the loss of impurities on the surface of the zeolite because of the activation process by means of calcination, after calcination the impurities that clog the pores of the zeolite will be separated and left the zeolite pores.

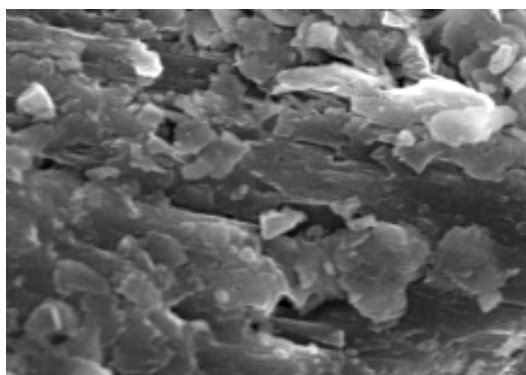


Fig. 3. SEM image of natural zeolite before activated (10000x of magnitude)

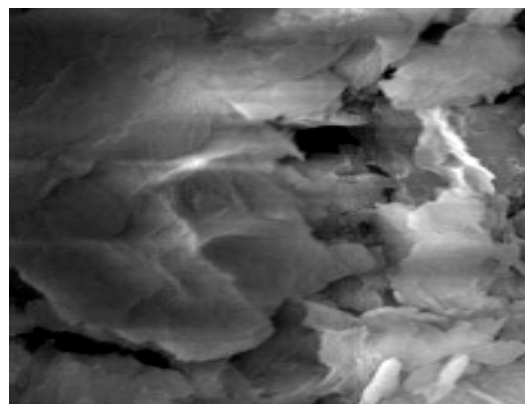


Fig. 4. SEM image of natural zeolite after activated (10000x of magnitude)

Table 3. BET Sorption Analysis Results

Adsorbent	Specific surface area (m^2/gr)	
	Before activation	After activation
Carbon	2	26
Natural zeolite	44	48

The BET analysis is commonly used for determining surface areas. Under the conditions of the BET measurement the N_2 molecules condense, filling the micropore volume. The BET surface areas calculated from the simulated nitrogen isotherms agree well with the accessible surface areas obtained directly from crystal structures in a geometric fashion. The BET sorption analysis results show in Table 3. Before activation, the carbon has a very small surface area which is only $2 \text{ m}^2/\text{g}$ compared to the surface area after activation which is of $26 \text{ m}^2/\text{g}$. To be an effective adsorbent, activated carbon must have a minimum surface area of $5 \text{ m}^2/\text{g}$ [7]. Here we can see that there is a considerable increase of the surface area after experiencing activation. In Table 3, the surface area of natural zeolite after activation has increased from 44 to $48 \text{ m}^2/\text{g}$. However, the increase in surface area obtained is not significant, possibly caused by improper use of the heating tool. Heating process should occur evenly on the entire surface of the zeolite so water molecules and organic substances impurities that exist on the surface of the zeolite can be optimally separated.

3.2 Effect of adsorbent height on phosphate removal

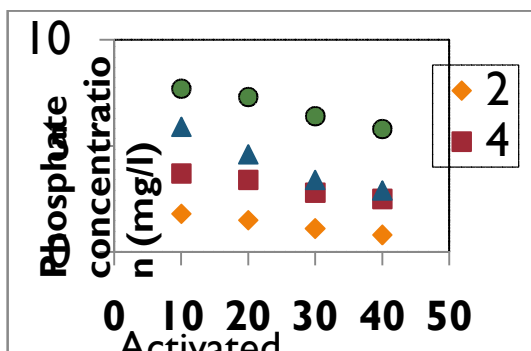


Fig. 5. Effect of activated carbon adsorbent height on phosphate removal

Figure 5 and 6 shows a graph of phosphate removal by using different adsorbent height of activated carbon and natural zeolite. The higher the adsorbent height, the higher phosphate content decreases. This shows that the higher the adsorbent height, the greater number of adsorbent were added and the larger active pores available so the higher the amount of phosphate could adsorbed.

As can be shown Figure 5, there has been a decrease in the amount of phosphate adsorbent ranging from a height of 10 cm, but the amount of phosphate adsorbed were not significant. It is proved that the activated carbon adsorption of the phosphate is low. The less optimal of activation process can lead to poor adsorption of activated carbon adsorbent.

At the highest activated carbon adsorbent height of 40 cm, final phosphate concentration of 0.8, 2.5, 2.9, and 5.8 mg/l were found by means of initial phosphate concentration of 2, 4, 6, and 8 mg/l, respectively as illustrated in Figure 5. The highest phosphate removal of 60% was obtained when applied the lowest initial phosphate concentration of 2 mg/l. This result is in agreement with Kilpimaa et al [8] who found the phosphate removal efficiency over the activated carbon residue decreased when the initial phosphate concentration was increased. This can be explained by the fact that optimal adsorption sites are occupied first at low concentrations. This phenomenon could be explained by the increasing of a driving force provided by the concentration gradient when the initial phosphate concentration in the solution increased.

Figure 6 displays that the decrease in phosphate concentration occurred from the natural zeolite adsorbent height of 10 cm, a decrease in the concentration of phosphate occurs quite significant when compared to the amount of original content. This proves that the natural zeolite has a high absorption of the phosphate.

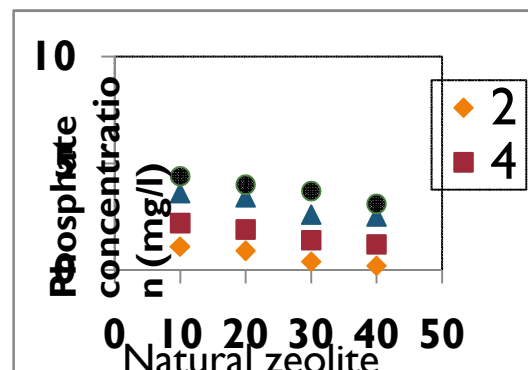


Fig. 6. Effect of natural zeolite adsorbent height on phosphate removal

The phosphate removal increases by increasing natural zeolite adsorbent height. It is can be said degradation of phosphate improved by increasing the amount of zeolite, as illustrated in Figure 6. The highest removal of phosphate by natural zeolite adsorbent was obtained at a height of 40 cm. This effect can be attributed to the greater amount of surface area and available binding sites of the adsorbent [9]. Other researchers found that an increase in adsorbent dose increased the removal of sulfate. The percent removal reached maximum of 97% at adsorbent doses of 800 mg/50 mL, for the minimum sulfate concentration of 20 mg/L [10].

At the highest natural zeolite adsorbent height of 40 cm, final phosphate concentration of 0.2, 1.2, 2.5, and 3.1 mg/l were found by means of initial phosphate concentration of 2, 4, 6, and 8 mg/l, respectively. The highest phosphate removal of 90% was achieved by using initial phosphate concentration of 2 mg/l. The highest phosphate removal was achieved at the lowest initial phosphate concentration. Similar results found by other researchers, whereas the highest ammonium removal efficiency was achieved at the lowest used initial ammonium concentration [4], and also the sulfate removal decreased as the sulfate concentration was increased [10]. This occurrence might be because of the higher concentration of adsorbate, the adsorbate



molecules become denser than the lower concentration of the adsorbate. This resulted in the adsorbent is more difficult to attract or adsorb these substances because it would require a larger absorption ability [11].

4. CONCLUSIONS

The natural zeolite was superior to degrade the phosphate compared to activated carbon. The highest decrease of phosphate by natural zeolite adsorbent was obtained when using the initial concentration of phosphate of 2 mg/l at a height of 40 cm adsorbent. A 90% degradation of phosphate was achieved.

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